

The University of Chicago

THE DETERMINATION
OF EXTREMELY SMALL TEMPERA-
TURE DIFFERENCES IN
CALORIMETRY

A DISSERTATION SUBMITTED TO THE FACULTY
OF THE DIVISION OF THE PHYSICAL SCIENCES
IN CANDIDACY FOR THE DEGREE OF DOCTOR
OF PHILOSOPHY

DEPARTMENT OF CHEMISTRY

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By
GALEN WOOD EWING

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THE DETERMINATION OF EXTREMELY SMALL TEMPERATURE
DIFFERENCES IN CALORIMETRY

In examining the behavior of solutions of electrolytes in high dilutions, heats of dilution can provide much important information.¹ However, the determination of such heats in very dilute solutions is rendered difficult on account of the small heats involved. The most precise measurements recorded in the literature have been made by Gucker,² Lange,³ Robinson⁴ and their respective co-workers, by means of low-resistance, multi-junction thermels.

By means of these thermels a temperature sensitivity of about 10^{-7} C.^o has been obtained, but it has not been feasible to work at concentrations much lower than 0.0025 molal.⁵ It would be possible to increase the sensitivity of the thermel by increasing the number of junctions or the cross-sectional area of the wires, were it not for the increased thermal conductivity accompanying such a change. The exact relations involved have been worked out by Ronneberg⁶ to give a "Merit Factor" for a thermel composed of any given pair of materials.

In the present research a survey has been made of various other possible means of measuring these small temperature differences, with a view to finding a method which would equal the multi-junction thermel in temperature sensitivity and at the same time avoid such a large heat loss through the measuring device.

¹Young and Seligmann, J. Am. Chem. Soc., **60**, 2379 (1939); Young and Gronier, J. Am. Chem. Soc., **58**, 187 (1936); Young and Machin, J. Am. Chem. Soc., **58**, 2254 (1936).

²F. T. Gucker, Jr., H. B. Pickard and R. W. Planck, J. Am. Chem. Soc., **61**, 459 (1939).

³Lange and Robinson, Chem. Rev., **9**, 89 (1931).

⁴Gulbransen and Robinson, J. Am. Chem. Soc., **56**, 2637 (1934).

⁵Young and Seligman, op. cit.

⁶C. E. Ronneberg, Ph.D. dissertation, Dept. of Chemistry, University of Chicago, 1935.

In the measurement of temperature differences as small as those in which we are interested, say 10^{-6} or 10^{-7} C.^o, it is necessary to use tools of the utmost sensitivity and to push them to the limit. Therefore it will be well to list those tools which are capable of high precision, and then to search for a method of applying them to the problem at hand.

1. Electromotive force measurements in low resistance d.c. circuits can be made with a precision of 10^{-9} volt by means of the White Potentiometer with a low resistance galvanometer. See Ronneberg's Ph.D. dissertation¹ for details.

2. Changes in the frequency of oscillation of a radio-frequency oscillator can be determined with a precision of about two parts in 10^8 by the method of beats. Such a change can result from changes in the constants of the resonant circuit, such as capacitance, inductance, resistance, and possibly other electrical quantities. When the conventional inductive-capacitive resonant circuit is employed, the frequency varies inversely as the square root of the product of the inductance and capacitance, when one assumes the resistance to be negligible. Then with the precision stated above, changes of the order of 4 parts in 10^8 in either the inductance or the capacitance could be considered the limit of measurement.

This minimum measurable change in capacitance can be used to determine changes in distance by means of the motion of one plate of a condenser, the so-called ultramicrometer principle. If one assumes a reasonable geometrical construction, a change in capacitance of 4 parts in 10^8 would correspond to a change in distance of only 10^{-7} cm. or about 10 Å. It should be noted that this figure is of the order of magnitude of molecular diameters, and that therefore it is doubtful whether some factor of uncertainty might not enter. Arenberg and Roope² have described an ultramicrometer which they state gives a sensitivity of 4 times 10^{-10} cm. per mm. of galvanometer deflection and "shows much higher sensitivity possible."

¹ Ibid.

² Arenberg and Roope, Phys. Rev., 53, 687 (1938).

Note that the limit of precision of the optical interferometer is of the order of half the wave-length of the light, and since light of wave-length less than $2000 \text{ \AA}$. could hardly be used, the limit of distance measurement would be about $1000 \text{ \AA}$. or 100 times larger than our calculation for the ultramicrometer.

3. High gain vacuum-tube circuits can be used to amplify small alternating currents or voltages, a voltage gain of 10^7 being within easy reach. Small changes in a constant voltage, such as that from a thermel or electromotive-force cell, may be amplified either by means of a direct-coupled amplifier (which is usually inconvenient) or by means of a commutator or some electronic method of modulation. The voltage gain of an amplifier is limited by the noise level due to thermal agitation of the electrons in the input resistor of the first stage. This noise can be reduced drastically by the use of a feedback circuit designed to pass all but a single pre-selected frequency and feed the rest back to a low level stage of the amplifier in such phase that they will be destroyed.¹ The single frequency then will be amplified selectively and only that component of the noise which is at the tuned frequency will get through to the output. This principle can be used to advantage in applications where only a single frequency is of interest.

SURVEY OF POSSIBLE TEMPERATURE MEASURING DEVICES

1. The first method to be investigated is the improvement of the thermel. Examination of the literature shows that germanium² and silicon³ have extraordinarily high thermoelectric powers, and of opposite sign. When the merit factors are computed according to the method of Ronneberg,⁴ they are found to be inferior to the iron-constantan couple, though superior to copper-constantan. The values are given in Table 1.

¹Scott, Proc. I. R. E., 26, 226 (1938).

²Bidwell, Phys. Rev., 19, 447 (1922).

³Wick, Phys. Rev., 25, 382 (1907).

⁴Ronneberg, op. cit.

TABLE I
PROPERTIES OF THERMEL PAIRS*

	E.m.f. deg. ⁻¹ junction ⁻¹	Merit factor x 10 ³
Iron, constantan.....	52.5 x 10 ⁻⁶	18.4
Silicon, germanium.....	740. x 10 ⁻⁶	17.6
Silicon, platinum.....	420. x 10 ⁻⁶	16.8
Copper, constantan.....	40. x 10 ⁻⁶	14.2
Germanium, platinum....	320. x 10 ⁻⁶	12.8

*The values of the thermal conductivities of Ge and of Si were estimated to be 5×10^{-3} cal. cm.⁻¹ deg.⁻¹ sec.⁻¹.

The oxides of lead and of bismuth (PbO and Bi₂O₃) have been reported¹ to have unusually high thermal e.m.f.'s at high temperatures. Preliminary calculations show that the merit factor of couples involving these oxides will be lower than 10⁻⁸, on account of the extremely high resistivity.

2. The temperature coefficient of linear expansion of a solid is commonly used as a measure of temperature change. If we assume a substance to change 50×10^{-6} of its length per degree, and assume a factor of 100 as mechanical advantage through the use of levers or similar devices, and assume a length of material of 10 cm., then the change in length will be 5×10^{-2} cm./deg., or 10⁻⁷ cm. for 2 microdegrees, which will be the ultimate limit of temperature sensitivity, when one uses the data for the ultra-micrometer calculated above.

3. The expansion of a gas according to Charles' Law may be used as a measure of temperature. If we assume a perfect gas, the change in volume will be proportional to the change in temperature. At a constant pressure the change in volume will be 1/300 of its value per degree at 27° C. If the volume is 10 cm.³, the change for one microdegree will be 3.3×10^{-8} cm.³. If an apparatus were so designed that this volume increment could be made to move one plate of a condenser as described above, the effect might be measurable, but it is difficult to conceive the construction of such an apparatus.

¹Bidwell, Phys. Rev., 3, 204 (1914).

4. The change in vapor pressure of a liquid in equilibrium with its vapor, as the temperature is changed, is large in the neighborhood of its critical temperature. Carbon dioxide has its critical temperature at 31.1°C . Its vapor pressure at 25°C . is about 63 atmospheres and changes at the rate of 1.5 atm./deg. Thus a change of one microdegree would mean a change in vapor pressure of about 10^{-3} mm. of Hg, which would be easily measurable by means of an oil manometer or otherwise. However, if we assume a volume of gas space above the liquid of 1 cm.^3 , then for a change of 1 microdegree, no less than 5.5 calories will be absorbed to vaporize the liquid. This is considerably greater than the total heat effect of most of the dilutions it is sought to measure, and hence the use of this material must be abandoned. The heat of vaporization at the critical temperature is zero, and close to the critical temperature is nearly zero, so if in the future a substance is discovered whose critical temperature is very close to 25°C ., this method might be feasible.

5. Callendar has claimed to have obtained a temperature sensitivity of 10^{-6} degree with his platinum resistance thermometer, though in the light of more recent knowledge, this would seem to be doubtful. Nevertheless, the resistance thermometer method is one of the most precise known.

Consider the Wheatstone's bridge circuit shown in Figure 1. All the arms are taken equal for simplicity, and arm BC is the temperature sensitive element. The increment of resistance in series with this arm due to the temperature change considered is dR . The expression for the unbalance voltage developed across AB due to an increment of temperature dT is

$$dE_{AB} = (EdR)/(4R + 2dR)$$

The increment dR will be negligible with respect to R , so we can write

$$dE = EdR/4R$$

E is the root-mean-square voltage across CD and is assumed to be independent of the resistance of the bridge. Thus for a large dE , we want E to be large and R small, though dR should be large.

If, now, we assume the use of a temperature-sensitive material with a change of 5 per cent per degree, and assume each arm of the bridge to be equal to 10^7 ohms., and $E = 10^3$ volts, and the amplification factor of the vacuum tube amplifier to be 10^6 ,

then the change in voltage output of the amplifier will be of the order of 10 volts per microdegree, which is very easily measurable.

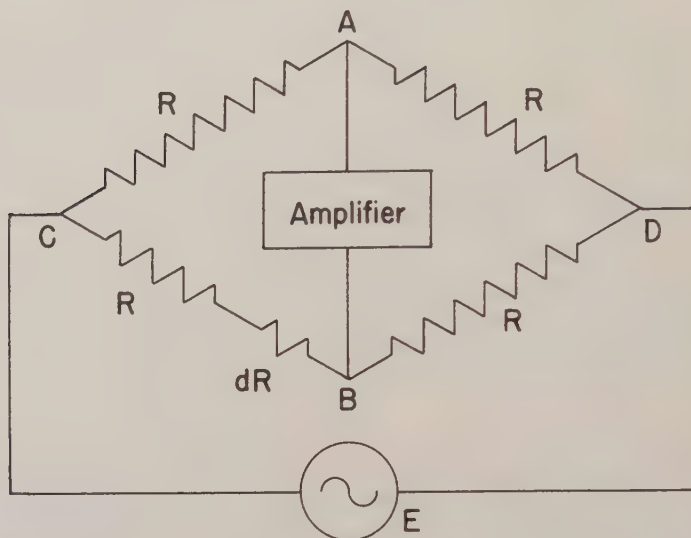


Fig. 1.--Wheatstone's Bridge

6. The temperature coefficient of the e.m.f. of a cell could conceivably be used as a measure of the temperature. For example, the cell $\text{Cu}/\text{Cu}^{++}/\text{Zn}^{++}/\text{Zn}$ changes by 0.023 volt per degree. It would appear quite possible to operate, say, 100 such cells in series, as for example, by filling a long, narrow, glass tube with alternate materials, like a miniature voltaic pile. It should be noted that a liquid junction is no disadvantage in this application, as it is not necessary to calculate the e.m.f. The method used for over-all calibration of the calorimeter and measuring device will include automatically any effects due to liquid junctions or polarization, so long as they are not a function of time. If 100 cells of the Cu-Zn reaction mentioned above are used in series, the sensitivity will be 2.3 microvolts per microdegree, which is well within the range of potentiometric measurements. In hunting for a cell reaction best suited for

this purpose, one should look for a reaction of high entropy change, ΔS , for

$$NF \, dE/dT = -d\Delta F/dT = \Delta S$$

in the Lewis and Randall nomenclature.

7. The magnetic properties of ferromagnetic substances vary with changes in temperature. For every such material, there is a range of temperature only within which the substance is ferromagnetic. The temperatures at which the magnetic properties are lost are very sharply defined, and are known as the upper and lower Curie points, respectively. For iron, the upper Curie point is at 785°C. , for nickel, somewhat higher. For small values of the magnetic field, the permeability increases with temperature, slowly at first and then more steeply, until at a temperature just below the Curie point it reaches a sharp maximum, from which it drops very abruptly, but with finite slope, to zero at the Curie point. For present purposes we are fortunate to have a ferromagnetic substance, manganese monophosphide (MnP), which shows its upper Curie point at about room temperature. It is reported by Hilpert and Dieckmann¹ that MnP loses its magnetic properties at 26°C. on heating, and regains them at 18°C. on cooling, though Mellor² has interchanged these two temperatures in his quotation. There is no temperature hysteresis unless the Curie point is included within the range of variation of temperature.

Insufficient data are available to permit even rough calculations of the temperature sensitivity possible by application of this phenomenon.

8. Certain piezoelectric crystals show properties which bear a rather close analogy to the magnetic properties of ferromagnetic materials.³ They possess an abnormally large dielectric constant in one particular crystallographic direction, and this passes through two very sharp maxima as the temperature is varied. These are known by analogy as the upper and lower Curie points, respectively. It so happens that the best known member of this

¹Hilpert and Dieckmann, Ber., 44, 2831 (1911).

²Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Longmans, Green and Co., New York, 1928, VIII, 853.

³Cady, Am. Phys. Teacher, 6, 227 (1938).

class of crystals, namely Rochelle salt (sodium potassium tartrate, sometimes known as Seignette salt), has its upper Curie point at 23.4°C ., 25°C . falling on the steep part of the curve. The lower Curie point is at -15°C . Refer to Figure 2, which is taken from Cady.¹

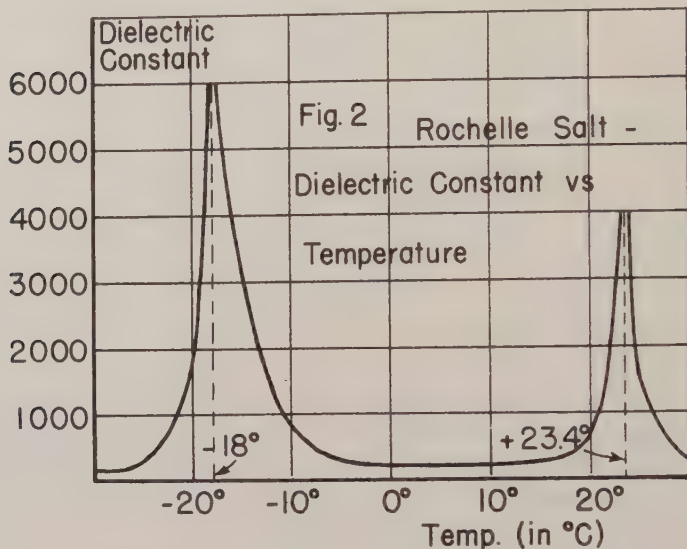


Fig. 2--Rochelle salt. Dielectric constant vs. temperature.

The dielectric constant of Rochelle salt in the X-direction reaches as high a value as 4000 at the upper Curie maximum, according to Cady,² and may go as high as 10,000 according to Zeleny and Valasek.³

If the limit of measurability of capacitance is taken as 4 parts in 10^8 , the value determined above, a change of 4 per cent per degree in the dielectric constant will correspond to a limiting temperature sensitivity of 1 microdegree.

¹Ibid.

²Ibid.

³Zeleny and Valasek, *Phys. Rev.*, **46**, 450 (1934); cf. also Bantle and Busch, *Helv. Phys. Acta*, **10**, 262 (1937).

9. Substances other than piezoelectric crystals have dielectric constants which change with the temperature. A search was made of the literature for such materials, and it was found that of all materials reported, nitrobenzene¹ appeared to be as practicable as any for present purposes. Its dielectric constant changes almost linearly over the range in which we are interested (-10 to +90° C.) with a coefficient of about 0.13 per cent per degree. This will not give greater sensitivity than about 50 microdegrees, which is insufficient.

EXPERIMENTAL PART

I. Resistance Coefficient

A search was made for substances of high temperature coefficient of resistance. Measurements were made on an a.c. Wheatstone's bridge designed according to Jones and Josephs.² The source of alternating current was an audio oscillator manufactured by the Clough-Brengle Company, Chicago, which was commonly operated at a frequency of 1000 cycles per second. The unbalance potential was amplified by a two-stage vacuum tube amplifier using type '30 triodes, detection by means of headphones. The material under test was placed in a suitable glass cell with platinum electrodes, in a water bath of about two liters capacity. A mercury-in-glass thermometer calibrated in tenths degrees Centigrade was inserted, as was an immersion heater of about 12 ohms. resistance, and an air-driven stirring propellor.

In each experiment the temperature was increased in intervals of degrees or less from a low temperature, usually about 12° C., to above 30° C. At each interval, time was allowed for the bath to come to approximate thermal equilibrium before the resistance was determined.

The values of resistance were divided by the value at 25° C., as determined from a smooth curve, to give relative values of resistance. The data for the various substances were plotted on the same sheet of coordinate paper, relative resistance vs. temperature (Figure 3). The material giving the steepest slope should be the most favorable for use in thermometry. The sign of the slope is of no consequence.

¹Abegg and Seitz, Z. für phys. Chem., 29, 242 (1899).

²Jones and Josephs, J. Am. Chem. Soc., 50, 1049 (1928).

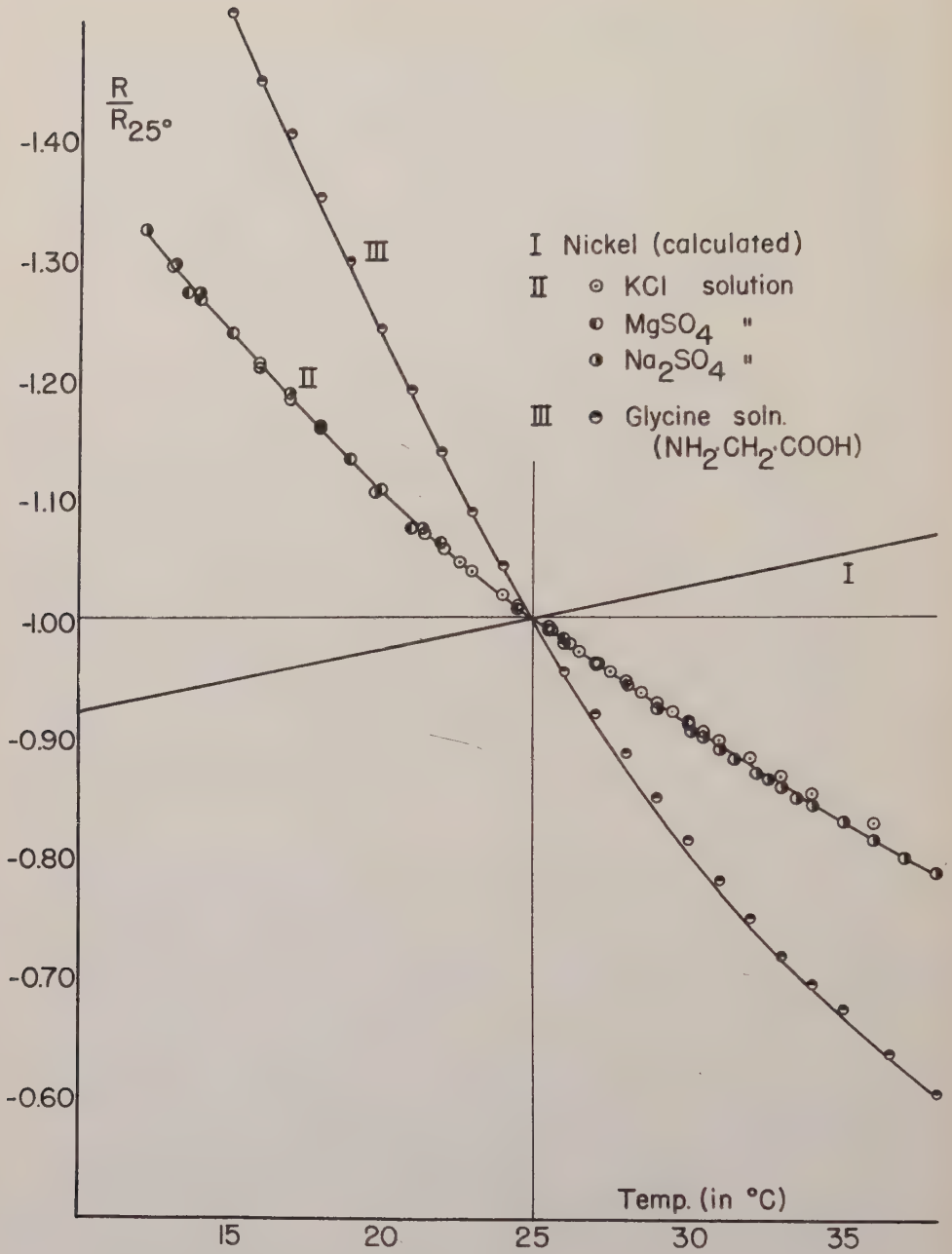


Fig. 3--Relative resistance vs. temperature

Since the data for metallic elements are given in the literature, it was not thought necessary to measure such materials. Aqueous solutions of strong electrolytes change their specific resistances by about 2 per cent per degree.¹ Experiments were made on sodium sulphate, potassium chloride, and magnesium sulphate solutions, also on benzoic acid, and glycine solutions.

The data for all these substances are summarized in Table 2.

TABLE 2
TEMPERATURE COEFFICIENTS OF RESISTANCE OF SUBSTANCES

Substance	Concentration	1/R(dR/dt)
Pt.....	pure	0.003
Ni.....	pure	0.006
Hytemco*.....	(special alloy)	0.0061
KCl solution.....	0.1 M	0.024
MgSO ₄ solution.....	0.01 M	0.024
Na ₂ SO ₄ solution.....	0.01 M	0.024
Benzoic acid solution.....	0.016 M (CO ₂ free)	0.016
Glycine solution.....	0.25 M	0.050

*Data supplied by the manufacturer, Driver-Harris Company.

II. Dielectric Constant Coefficient

An apparatus for the measurement of dielectric constants by the resonant method was constructed as follows. Two identical oscillators were built, using type 24A tetrodes in an electron-coupled Hartley circuit. The frequency of each was controlled by the resonance of a coil with two parallel capacitances, the capacitance of a condenser with the material under test as dielectric and that of a small variable air condenser.

The high frequency outputs from these oscillators were led to the two control grids of a 6L7 mixer tube, the frequency of the output from which was equal to the difference between the frequencies of the two oscillators. This was in turn amplified by a

¹H. S. Taylor (ed.), "A Treatise on Physical Chemistry," D. Van Nostrand Co., New York, 1930, Vol. I, p. 670, n. 2.

single 6L7 stage and fed to the vertical deflection system of a cathode ray oscillograph. The horizontal deflection plates of the oscillograph were supplied with a sine-wave e.m.f. at the frequency of the city power supply, 60 cycles. A schematic diagram of the apparatus is shown in Figure 4, and a detailed circuit diagram of one oscillator and the mixer in Figure 5.

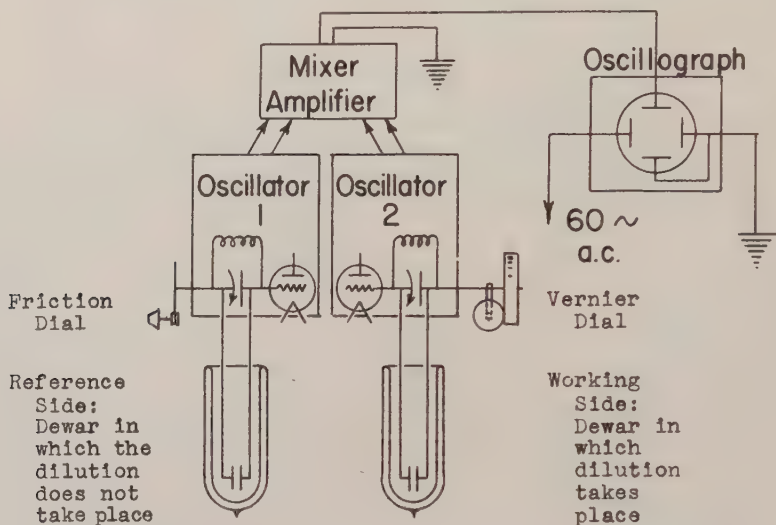


Fig. 4--Dielectric constant apparatus; schematic diagram

Referring to Figure 4, it is seen that each oscillator is controlled by a condenser immersed in a Dewar flask calorimeter. In one of these Dewar flasks (No. 2) is also to be located the dilution pipette. Both flasks are stirred by propellers geared to the same synchronous motor, and contain heaters for calibration purposes. By this duplicate method any change in temperature which affects both calorimeters equally, such as a change in the temperature of the external thermostat, or heat input due to stirring, will cancel out and not appear in the final results. However, any heat effect taking place in one Dewar to the exclusion of the other, i.e., the heat of dilution, will change the frequency of the corresponding oscillator only, and this frequency change, not being balanced by one on the other side, will show up in the heterodyne frequency in the mixer circuit.

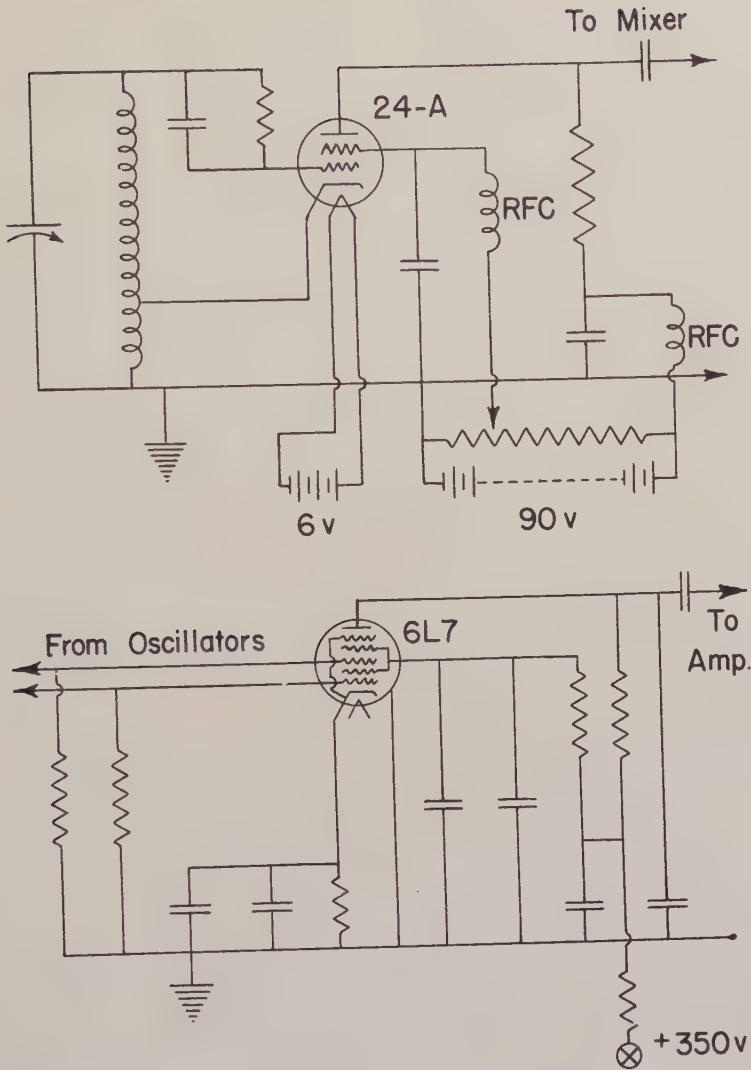


Fig. 5--Dielectric constant apparatus; oscillator above, mixer below.

In actual construction, each oscillator with its coil and variable condenser was mounted separately in a box of heavy sheet copper with corners of angle duralumin. The variable condenser

of oscillator No. 2 was driven by a precision vernier dial with a slow motion device, No. 1 by a radio type friction-drive dial.

The test condensers (to be described below) were connected to the oscillators by lengths of flexible coaxial cable with insulation of a polystyrene resin. This cable, which is manufactured by the American Phenolic Corporation, has a very low capacitance per unit length, and an extremely low dielectric loss at high frequencies. The high frequency leads from the oscillators to the mixer unit were also made of shielded cable, and care was taken to shield the two grid leads of the 6L7 from each other, to avoid any possibility of a frequency change in one oscillator affecting the frequency of the other. In the final assembly, it was found that the two oscillators would not lock together in frequency until their difference of frequency was less than 5 cycles per second.

The oscillation frequency in the majority of these experiments was 1 megacycle per second within about 10 per cent.

The oscillator tubes were heated by current from a six-volt storage battery, the two tubes being in series, with the mid-point connected to ground. The plate voltages were taken from a single 90-volt "B" battery, the screen voltages from a potentiometer across the same battery. With such an arrangement it is possible to find a point in the potentiometer setting such that a variation in the total battery voltage will have minimum effect on the frequency of oscillation. The voltages for the mixer and amplifier stages were obtained from a stabilized rectifier unit.

The two oscillators in their copper shields and the mixer were mounted in an inverted position immediately above a large constant-temperature water bath, so that the leads from oscillators to calorimeter might be as short as possible. The structure on which these units were mounted was supported from the floor independently of the water bath foundation, to minimize vibration from the stirring motors. Sponge rubber cushions were also used. The air space surrounding the oscillators above the water bath was enclosed with a frame of wallboard, so that the air temperature would remain fairly constant.

It should be noted that for purposes of temperature measurement, it is not necessary to calculate the actual dielectric constants, the change in the capacitance of the variable condenser needed to maintain a constant frequency difference between the oscillators will be proportional to the change in dielectric

constant of the medium in the test condensers. It is generally desirable to treat the time as the independent variable, and plot capacitance as function of time. By examination of such a plot in the present apparatus, one can deduce the behavior of the temperature, also as a function of the time.

In the course of this investigation, numerous experiments were made to determine the temperature variation of dielectric constant of various samples of Rochelle salt crystals. The component of dielectric constant which is of interest is that in the X-direction of the crystal. This is the direction which must be in the thickness dimension of crystals prepared for piezoelectric uses, so it may be concluded that sections intended for such use would also be suitable for present purposes. Following this plan, a series of experiments was performed on crystal units such as are commercially available for use in phonograph pick-ups. These are "bimorphs," that is, pairs of crystals cut in the same direction, in thin slices, then rotated with respect to each other through such an angle that when an electric field is applied across the thickness dimension, a torsional stress will be developed. The slices are then cemented together with thin foil electrodes on each side of each slice, the outer two and the inner two being connected together, respectively.

For these experiments the bimorph unit enclosed in a brass housing was connected to the oscillator (No. 2) by means of coaxial cable. No test condenser of any sort was connected to oscillator No. 1. The temperature in the calorimeter No. 2 was varied over a considerable range by the addition of ice or heat as required, and the vernier dial adjusted as necessary to keep the difference of frequencies constant, and in this case equal to zero rather than to 60 cycles.

The curve obtained for capacitance dial setting vs. temperature for this sample was linear over the range 23.2° to 25.2° C. with a slope of about 7 per cent per degree, decreasing with increased temperature.

Similar experiments were made using a single crystal cut from a large piezoelectric slab. This single piece was about two square millimeters in area and 0.8 mm. thick, with foil electrodes on the two surfaces. Connection was made to these electrodes by means of two thin strips of sheet silver with a pad of rubber arranged to exert a small pressure against the silver to ensure good

contact. A copper-constantan thermo-junction was cemented to the edge of the crystal to measure the actual temperature. The whole was enclosed in a brass capsule as before and immersed in the calorimeter.

Curves for different samples prepared in this way were found to differ greatly in their form and slope. They did not (in general) show a very definite minimum at approximately 23.4°C ., corresponding to the maximum expected in the dielectric constant at the Curie temperature. However, the slopes were frequently very steep over limited ranges and were reproducible on the same sample from day to day. The steepest slope recorded corresponded to a change in dial setting of approximately 200 per cent per degree over the range 23.2 to 23.35°C .

It seemed possible that these inconvenient differences between the temperature curves of the various crystal samples could be ironed out by using a great many crystals simultaneously, to wit, a powder. The effective dielectric constant should be one-third of that in the X-direction, since the constant in the other two directions is negligible as compared with it, and the temperature variation should be proportional. A sample of reagent grade Rochelle salt was ground as fine as possible in a mortar and packed into a brass cylindrical capsule equipped with an insulated central wire projecting into the pressed powder mass. Similar curves were determined for this sample as for the previous. Contrary to expectation, the powder showed an almost linear change with temperature over the range 13.5 to 25.0°C ., with a slope of only about 1.9 per cent per degree.

Some experiments were carried out using nitrobenzene as the temperature sensitive material. This material was chosen after a search of the literature had been made for a liquid material which would be easily handled and would change its dielectric constant with temperature as much as possible. A curve of capacitance against temperature was determined for this substance in the same way described above. A slope of about 0.5 per cent per degree was obtained over the range 21 to 25°C . This is in quite good agreement with the value of 0.6 per cent per degree for the change of dielectric constant as given in the literature.¹

It was desired to determine whether or not the heat produced in the dielectric itself would be so large as to be

¹Abegg and Seitz, op. cit.

objectionable. Two identical brass capsules were constructed to serve as condensers to be filled with nitrobenzene. One was mounted in each side of a divided calorimeter, into the partition of which was built a 400-junction thermel of copper and constantan (used by J. Gall¹). For the first experiments, one only of these condensers was connected to the corresponding oscillator, the other capsule being left in place to equalize stirring conditions. A slight heat effect was noticed when the oscillators were turned on, about 40 microwatts input being the maximum observed. In one experiment the stirring was disconnected in one side of the calorimeter. The heat of stirring was found to be at least 20 times as large as that due to the oscillation. Since the heat of stirring presents no insurmountable problem it is evident that the present proposed method for measuring temperature differences will not be ruled out on account of heat produced in the measuring device. There seems no reason to suppose that very different results will be found in similar experiments with Rochelle salt, though such have not been made.

With a test condenser on one side only of the calorimeter, the system reached thermal equilibrium with a difference of temperature between the halves about 6.6×10^{-4} C.^o different from what it would have been with oscillators turned off. With condensers on both sides, however, this figure was reduced by 50 per cent. It is evident that if careful adjustment were made to equalize the amount of heat dissipation in the two condensers, this difference could be reduced to as small a value as desired.

Thus it is concluded that the change in dielectric constant of Rochelle salt with temperature will provide a possible method for precise temperature measurement. The difficulties will undoubtedly lie principally in obtaining samples of crystal having the desired electrical properties.

CONCLUSIONS

Of the possible methods for the measurement of very small temperature differences considered, the following will apparently give sufficient sensitivity for the purpose in hand.

¹J. Gall, Ph.D. dissertation, Dept. of Chemistry, University of Chicago, 1939.

1. The resistance thermometer bridge.
2. The temperature coefficient of e.m.f. of a cell.
3. The temperature dependence of dielectric constant of Rochelle salt.
4. Possibly the temperature dependence of permeability of manganese phosphide.

